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*MEMORANDUM REPORT ARCCB-MR-90010*

# *DETERMINATION OF SODIUM CYANIDE IN COPPER AND CADMIUM CYANIDE PLATING SOLUTIONS BY PRECIPITATION-FORMATION TITRATION*

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The chemical literature lacks an acceptable analytical method to adequately determine and monitor sodium cyanide in copper and cadmium cyanide plating solutions in the plating processes. In this report, an improved method is presented providing acceptable analysis and monitoring of this salt in these plating processes. The optimum operating ranges of sodium cyanide are 58 g/l maximum in copper cyanide plating solutions and 149 g/l maximum in cadmium cyanide plating solutions. The resulting precisions are in the range of

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20. ABSTRACT (CONT'D)

0.5 to 4.0 g/l, providing adequate monitoring of these metal finishing solutions supported by six years of testing.

## TABLE OF CONTENTS



### TABLES

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## INTRODUCTION

The chemical literature lacks an acceptable analytical method to determine and monitor sodium cyanide in copper and cadmium cyanide plating solutions in the plating processes. Lack of optimization of these plating solutions causes serious problems for the metal finishing industry such as poor quality products and wasted resources.

The only common chemical analysis method to determine sodium cyanide in these solutions is a color comparison test kit such as the one provided by Merck Corporation (ref 1), however, this method provides poor precisions.

The specific method described in this report provides acceptable analysis and monitoring of this salt in the metal finishing processes. The method consists of a precipitation-formation titration (refs 2,3). Relative precisions of this method are in the range of 2 to 3 percent.

## EXPERIMENTAL PROCEDURE

Strict analytical chemistry methods and procedures are followed throughout this experimental procedure section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 3).

Two analytical reagent grade standard solutions are required. The first is a 50 $\pm$ 0.5-g/l sodium cyanide solution (1 g/l sodium hydroxide for stabilization), and the second is a 17 $\pm$ 0.1-g/l silver nitrate titrant solution. These two solutions are prepared and standardized as described in References 2 and 3.

Two other analytical reagents are required. The first is potassium iodide indicator powder and the second is concentrated ammonium hydroxide solution.

The procedure to prepare standard and sample solutions is the same for the copper and cadmium cyanide solutions. This titration analysis requires that 2 milliliters (ml) of sample or standard solution is pipetted into a 400-ml

beaker. Then the beaker is filled to about the 100-ml mark with deionized water and a stirring bar is added. Also added to this beaker is 0.1 gram of potassium iodide indicator and 5 ml of concentrated ammonium hydroxide solution.

The solution is titrated using the silver nitrate titrant to a faint yellow turbid permanent endpoint, recording the amount of titrant dispensed in milliliters at the endpoint.

All standard and sample solutions are analyzed in triplicate. Sodium cyanide concentrations in the samples are calculated by normal chemical stoichiometry.

## RESULTS AND DISCUSSION

Experimental standard titration data are presented in Table I for these solutions. Experimental sample titration data are presented in Table II for copper cyanide sample solutions one and two and in Table III for cadmium cyanide sample solutions three and four. The titration can be summarized using the following equations. The first two involve the cyanide-silver ion relationship and the third involves the iodide-silver ion endpoint indicator relationship:

$$Ag^+ + 2CN^- \text{ <--> } (Ag(CN)_2)^- \quad (1)$$

$$(Ag(CN)_2)^- + Ag^+ \text{ <--> } 2AgCN \quad (2)$$

$$Ag^+ + I^- \text{ <--> } AgI \quad (3)$$

Silver cyanide will not precipitate in these solutions due to the presence of ammonium ions allowing only the silver iodide to precipitate at the endpoint.

The calculation for determining the concentration of sodium cyanide in the original sample solutions is

$$g/l\ NaCN = (50)(A)/(B) \quad (4)$$

where

A = ml of titrant for sample

B = ml of titrant for standard

where the constant value in Eq. (4) is the combined result of many constants (refs 2,3).

Using Eq. (4), the respective sodium cyanide values for copper cyanide sample solutions one and two in Table II are 35.1 and 49.9 g/l. Likewise, using the same equation, the respective sodium cyanide values for cadmium cyanide sample solutions three and four in Table III are 84.9 and 140.1 g/l.

It is useful to evaluate the variations in precision for the materials and methods used. Tables IV through VII present the data for the 2-ml class-A pipets, 50-g/l sodium cyanide standard solution, 17-g/l silver nitrate titrant solution, and the 50-ml class-A burets, respectively.

The data obtained by this method are sufficient to adequately monitor the sodium cyanide in the metal finishing processes, thus providing efficient use of resources. The optimum operating ranges of sodium cyanide are 58 g/l maximum in the copper cyanide plating solutions and 149 g/l maximum in the cadmium cyanide plating solutions. The resulting precisions are in the range of 0.5 to 4.0 g/l, providing adequate monitoring of these metal finishing solutions supported by six years of testing.

## REFERENCES


1. "EM Quant Chlorine and Cyanide Tests," EM Science Division of Merck Corporation, Cherry Hill, NJ, 1980.

2. D. Peters, J. Hayes, and G. Hieftje, Chemical Separations and Measurements: Theory and Practice of Analytical Chemistry, W. B. Saunders Company, Philadelphia, PA, 1974.

3. J. Fritz and G. Schenk, Quantitative Analytical Chemistry, Fifth Edition, Allyn and Bacon, Inc., Boston, MA, 1987.

TABLE I. EXPERIMENTAL TITRATION DATA FOR THE SODIUM CYANIDE STANDARD SOLUTION

| Replicates | Titrant Used (ml) |
|---|---|
| 1 | 10.25 |
| 2 | 10.20 |
| 3 | 10.20 |
| X(avg) | 10.22 |

TABLE II. EXPERIMENTAL TITRATION DATA FOR SODIUM CYANIDE IN COPPER CYANIDE SAMPLE SOLUTIONS

| Replicates | Sample One Titrant Used (ml) | Sample Two Titrant Used (ml) |
|---|---|---|
| 1 | 7.15 | 10.20 |
| 2 | 7.15 | 10.20 |
| 3 | 7.20 | 10.20 |
| X(avg) | 7.17 | 10.20 |

TABLE III. EXPERIMENTAL TITRATION DATA FOR SODIUM CYANIDE IN CADMIUM CYANIDE SAMPLE SOLUTIONS

| Replicates | Sample Three Titrant Used (ml) | Sample Four Titrant Used (ml) |
|---|---|---|
| 1 | 17.35 | 28.60 |
| 2 | 17.35 | 28.65 |
| 3 | 17.35 | 28.65 |
| X(avg) | 17.35 | 28.63 |

TABLE IV. PRECISION OF A 2-ml CLASS-A PIPET

| Replicate | 2-ml Pipet Volume (ml)* |
|---|---|
| 1 | 2.00 |
| 2 | 2.01 |
| 3 | 1.99 |
| 4 | 1.99 |
| 5 | 1.99 |
| 6 | 2.01 |
| X(avg) | 2.00 |
| Sn | 0.01 |

*Volumes are calculated from the weight-volume relationship of a pipetted deionized water solution corrected for temperature.

TABLE V. PRECISION OF A 50-g/l SODIUM CYANIDE STANDARD SOLUTION

| Replicate | Sodium Cyanide (g/l)* |
|---|---|
| 1 | 49.97 |
| 2 | 49.99 |
| 3 | 49.99 |
| 4 | 50.01 |
| 5 | 50.00 |
| 6 | 50.02 |
| X(avg) | 50.00 |
| Sn | 0.02 |

*Sodium cyanide concentrations are calculated by methods given in References 2 and 3.

TABLE VI. PRECISION OF A 17-g/l SILVER NITRATE TITRANT SOLUTION

| Replicate | Silver Nitrate (g/l)* |
|---|---|
| 1 | 17.1 |
| 2 | 17.0 |
| 3 | 17.2 |
| 4 | 16.8 |
| 5 | 16.9 |
| 6 | 16.8 |
| X(avg) | 17.0 |
| Sn | 0.2 |

*Silver nitrate concentrations are calculated by methods given in References 2 and 3.

TABLE VII. PRECISION OF A 50-ml CLASS-A BURET

| Replicate | Volume (ml)* |
|---|---|
| 1 | 24.94 |
| 2 | 24.98 |
| 3 | 25.02 |
| 4 | 25.05 |
| 5 | 24.98 |
| 6 | 25.05 |
| X(avg) | 25.00 |
| Sn | 0.04 |

*Volumes are calculated from the weight-volume relationship of a contained deionized water solution corrected for temperature at a point one-half full--25 ml.

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